

Metal-insulator transition in VO_2 : a Peierls-Mott-Hubbard mechanism

Xiangyang Huang, Weidong Yang, and Ulrich Eckern

Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany

(February 1, 2008)

Abstract

The electronic structure of VO_2 is studied in the frameworks of local density approximation (LDA) and LDA+ U to give a quantitative description of the metal-insulator (MI) transition in this system. It is found that, both structural distortion and the local Coulomb interaction, play important roles in the transition. An optical gap, comparable to the experimental value has been obtained in the monoclinic structure by using the LDA+ U method. Based on our results, we believe that both, the Peierls and the Mott-Hubbard mechanism, are essential for a description of the MI transition in this system.

The observation of a metal-insulator (MI) transition in VO_2 has attracted much interest for several years. Actually, this material has been considered a prototype of transition-metal oxides with an interesting MI transition. The transition occurs at temperature about 340 K with a cell-doubling phase transition from the rutile to the monoclinic structure, its conductivity jumping by more than five orders of magnitude [1]. The transition is associated with a small change in volume, but significant internal atomic rearrangement characterized as both a pairing and an off-axis displacement of alternate vanadium atoms. In its insulating phase, VO_2 has no magnetic order. The discovery of this transition initiated several experimental [2–5] and theoretical investigations [6–11], trying to explain the explanation of the mechanism of this phenomenon.

It is commonly accepted that Peierls and Mott-Hubbard pictures are two main mechanisms for MI transitions in half-filled band systems. Since VO_2 is of a half-filled band type, and possesses both a structural transition as well as a significant Coulomb interaction (U) in the $3d$ bands of vanadiums, the question arises which mechanism drives the transition. This problem has been debated for nearly four decades, and continues to be a controversy. An early attempt was given by Goodenough [6], who, due to the existence of V-V pairings in the monoclinic structure, argued the transition to be of Peierls type: in his point of view, the V-V pairing and the pronounced octahedral distortion are responsible for the insulating state, and the gap is solely determined by the crystalline distortion. Somewhat later, Zylbersztejn and Mott proposed another model [7]. With the information obtained from the properties of $\text{V}_{1-x}\text{Cr}_x\text{O}_2$, they argued that the band gap should essentially be due to the Hubbard mechanism. Nevertheless, both of the two models are based on qualitative analysis and have not offered us a satisfied scenario of the MI transition.

Many theoretical efforts have been made to give a quantitative description of the MI transition in VO_2 from first-principles calculations. Earlier works include a semiempirical band study by Caruthers et al. [8] and a cluster calculation on V-O octahedrons by Sommers et al. [9]. Most noticeable, in 1994, an *ab initio* molecular dynamics (MD) study on VO_2 performed by Wentzcovitch et al. [10] gave a good description to the structural performance

of VO_2 , in which V-V pair distances along the c-axis in the monoclinic phase are further reduced from the experimental value. However, their calculated optical gap of -0.04 eV contradicts the observed value of 0.7 eV [2]. A recent study based on the augmented spherical wave (ASW) method within the atomic sphere approximation (ASA) gave nearly the same band picture of electronic structure [11].

Thus up-to-date results from LDA and other calculations can not provide a satisfactory quantitative description to the MI transition in VO_2 . We suspect that this failure is mainly due to the neglect of the local Coulomb interaction, which may be significant in 3d transition oxides. Since no full potential, all-electron calculations, and no quantitative study considering a finite Coulomb interaction U have been reported so far, the driving mechanism is still unclear, and a comprehensive study with taking into account both effects is in order. In this article, we propose to study the mechanism of the MI transition in VO_2 by using the LDA as well as the LDA+ U method [12,13]. The latter has been proved to be an efficient and reliable tool to study systems with strong Coulomb interactions. Our results show that both, lattice distortion, and Coulomb interaction play important roles in the transition. It seems that correct and quantitative description can not be obtained without taking into account either of them.

Our calculations are based on density functional theory within LDA and LDA+ U . The LDA calculations are performed in the full-potential linearized augmented plane-wave method (FP-LAPW) with local orbital extensions [14], and the full-potential linear muffin-tin orbital approach (FP-LMTO) [15], while LDA+ U calculations [13] are carried out within the framework of the FP-LMTO approach [15]. The non-overlapping muffin-tin spheres are adopted in both approaches. For the FP-LMTO approach, three κ 's basis sets, -0.1, -1.0, and -2.5 Ry, are chosen. The potential is expanded in spherical harmonics inside the sphere, and Fourier transformed in the interstitial region. Therefore, no shape approximations are made to the density or potential. In both methods, the calculated results are checked for convergence with respect to the number of \mathbf{k} points and the plane wave cutoff energy. In the LDA+ U method, the screened U parameter used are ranging from 1.2 eV to 5.0 eV,

which have been suggested by different authors, and are reasonable in early transition oxides [2,5,16,17]. The screened J is estimated to be $0.12 U$.

Our calculations have been carried out in the rutile structure of VO_2 (space group $P4_2/mnm$) as well as in the monoclinic M_1 structure (space group $P2_1/c$). The lattice parameters for these two structures used in our work are taken from McWhan et al. [18] and Longo et al. [19], respectively. In contrast to previous band calculations, our calculations were performed with full-potential methods.

The densities of states (DOS) of the two structures, as determined by the LDA calculation, are shown in Fig. 1. It can be seen from Fig. 1(a) that the DOS in the metallic phase near the Fermi level is contributed mainly from vanadium $3d$ states, which are split by the octahedral field into two groups, a lower triply degenerate state of t_{2g} , and an upper doubly degenerate state of e_g . The degeneracy of t_{2g} (e_g) is further eliminated due to the orthorhombic field. Two distinct changes are obvious when comparing the two phases. One is an upward shift of so-called π^* bands (d_{xz} and d_{yz}) above the Fermi level, the other is a splitting of the $d_{||}$ band (d_{xy}) of about 1.7 eV. We argue that the former change is mainly caused by the V-V pairing. According to our calculation, the shifts of d_{xz} and d_{yz} band are about 0.18 and 0.27 eV with respect to the rutile phase, respectively. The occupation number of the π^* band is reduced from 0.45 e/atom in the rutile phase, to 0.15 e/atom in the monoclinic phase. These two effects greatly eliminate band crossings, and lead to a reduction of the DOS at the Fermi level (see Fig. 1(b)). Our calculations are in qualitative agreement with Goodenough's model [6] and quantitatively confirm the recent results by Eyert [11]. The results obtained from the *ab initio* MD gave a smaller overlap of bands near the Fermi level than ours: in the MD calculation, the potential adopted is a pseudo one and the parameter used is theoretically optimized, i.e. the c-axis V-V pairing has been reduced from the experimental value of 2.62 Å to 2.58 Å.

Our calculations show, confirming a suggestion by Eyert [11], that further reducing the V-V pairing to ~ 2.50 Å even produces a non-overlap band structure; which even though the value is unrealistic, it is an interesting observation in itself. Our FP-LAPW

calculations also show that artificial reduction of V-V pairing have raised the total energy of the monoclinic phase comparing to that of the experimental lattice parameter. Specifically, the total energy in the experimental parameter is calculated to be of ~ 6 mRy/molecule lower compared to the case when the optimized value is used [10]. We also used the generalized gradient approximation (GGA) to calculate the band structure of VO₂, with essentially no improvement. We conclude that the structural distortion plays an important role in MI transition in VO₂, and it strongly alters the band structure of the insulating phase near the Fermi level. The upward shift of the π^* and the separation of the upper $d_{||}$ band from the lower $d_{||}$ band caused by the V-V pairing leaves the lower $d_{||}$ band nearly filled. Even so, it can only lead to a reduction of carriers (or a small gap) near the Fermi level. The electronic properties of VO₂ in the insulating state, therefore, can not be described by a LDA band calculation. A significant improvement is obtained, as we demonstrate below, by supplementing the LDA by a local Coulomb term U .

In order to get a better picture of the MI transition in VO₂, we go beyond the LDA and check the part of correlation played in this system. The band structure of VO₂ in the insulating phase has been computed by the LDA+ U method, and is shown in Fig. 2. [$U=0$ represents the result for LDA.] We see that the band structure of the monoclinic phase is indeed modified by U . The Coulomb interaction U has two effects on the band structure, see, for example, Fig. 2(b): the first effect is to cause a dramatic shift of the π^* band from the lower $d_{||}$ band for ~ 0.7 eV, the other one is to cause a further separation of the $d_{||}$ bands. The former effect is responsible for opening a gap; the latter one is not so important since the separation of the $d_{||}$ band by the structural distortion has been large enough, i.e., greater than the optical gap of 0.7 eV. Notice that this can only be achieved on the basis of the structural distortion. To illustrate this point of view, we have performed a LDA+ U calculation on the metallic structure of VO₂, with the result that a gap is not opened by a value of U up to 7 eV. In this case, the overlap of the π^* and the $d_{||}$ band has not been eliminated, and the $d_{||}$ band near the Fermi level is still of a half-filled type. Further increasing U is not reasonable in this system. This clearly indicates that the metallic phase

is determined by the structure, and can be adequately understood by LDA theory.

By varying U in the reasonable range from 0 eV to 5 eV in the insulating phase of VO_2 , we obtain gap values from -0.17 eV to 0.96 eV. The band gap as a function of the Coulomb interaction U is displayed in Fig. 3. [A negative gap represents an overlap of the $d_{||}$ and the π^* bands near the Fermi level.] A gap is opened, and exhibits roughly a linear relationship with U in the range of U between 1.6 eV and 5 eV. Specially, for $U=4$ eV, our calculation gives a gap of 0.67 eV, which is in good agreement with the experimental value of 0.7 eV. It is instructive and necessary to apply the LDA+ U method to MoO_2 and check whether this method are valid in our study. Although MoO_2 crystallizes in the same monoclinic structure as low temperature VO_2 , it is still metallic. The LDA+ U band calculations [20] shows that the lower $d_{||}$ band is completely occupied, and that the Fermi level is located in the lower-middle part of the π^* band. This condition is quite different from low temperature VO_2 . Since the overlap of bands near the Fermi level is about 1 eV, even a rather large U (up to 6.0 eV) can not open a gap in this system. This explains well why MoO_2 is a still metal in spite of large U values.

Figure 4 shows the calculated DOS by LDA+ U compared with the ultraviolet photoemission spectroscopy (UPS) spectrum [2] in the insulating phase of VO_2 . The UPS spectrum clearly shows that the $2p$ and $3d$ band are in the energy range of -2 to -9 eV, and 0 to -2 eV, respectively. We find that there is an overall good agreement between experiment and theory, with the exception of an underestimation of the $3d$ downshift by about 0.9 eV. Also, the calculated DOS fits well with the x-ray photoemission spectroscopy (XPS) and UPS spectra by Goering et al. [3] and Bermudez et al. [4] First, the calculated DOS drops to zero at the Fermi level, which well explains the structure of UPS spectrum near the Fermi level. Second, the three peaks in the DOS curve centered at about -3.5 eV, -5.2 eV, and -7 eV are in good agreement with the O $2p$ structure in the UPS spectra. We also compared our result with the O $1s$ x-ray absorption spectroscopy (XAS) spectra [21] which reflects the unoccupied states. The three peaks of π^* , $d_{||}$ and σ^* can also be well explained by our DOS results.

Further discussion about $3d$ transition oxides such as TiO_2 and CrO_2 will help us to understand the MI transition in VO_2 . It is interesting to note that the above oxides in rutile structure exhibit different properties, i.e., TiO_2 is an insulator, VO_2 undergoes a MI transition and CrO_2 is a semi-metal. A simple model derived from the band picture can give a good explanation. There are two MO_2 ($\text{M}=\text{Ti}, \text{V}, \text{Cr}$) units per cell in each system while the numbers of occupied valence electrons in the $d_{||}$ bands are quite different. In TiO_2 , since the O $2p$ orbitals are filled, the zero number of d electrons leave unoccupied d bands above Fermi level and cause an insulating phase. This is quite different from the case of VO_2 . There are two half-filled bands near the Fermi level which can not be split by a rather large value of U . This situation can be changed by cell-doubled distortion during the MI transition. In the insulating phase there are four VO_2 molecular per cell which nearly fills the lower $d_{||}$ bands. According to this picture, one may expect CrO_2 to be an insulator since the two bands near the Fermi level are fully occupied by four electrons, and the Coulomb interaction will separate these bands from other d bands. However, the ferromagnetic mechanism will account for the semi-metal property [22,23].

In conclusion, the band structure of VO_2 is calculated with the LDA and LDA+ U methods. Our results show that both, lattice distortion and Coulomb interaction, play important roles in the MI transition in VO_2 . First, the distortion strongly alters the band structure of the low temperature monoclinic phase relative to that of the high temperature rutile phase. It induces a small overlap of bands at the Fermi level but still leaves the system to be metallic. Second, the Coulomb interaction further splits the π^* bands from Fermi level via the Mott-Hubbard mechanism. This cooperative effect causes an optical gap and thus the MI transition. With a reasonable value of $U \sim 4$ eV, we obtain a gap of 0.67 eV, which is close to that observed in experiment. A similar calculation is also performed in the rutile phase. There, no gap is found for U up to 7 eV. In conclusion, neither the Peierls nor the Mott-Hubbard mechanism provides a comprehensive picture of the transition. Our calculation indicates that it is rather a combination of both, which gives a quantitative description of the metal-insulator transition in VO_2 .

One of us (XH) acknowledges useful discussions with Prof. Y. Wang, as well as financial support by the Alexander von Humboldt-Stiftung. We are grateful to Dr. S. Y. Savrasov for providing his FP-LMTO code. This work was supported by the Deutsche Forschungsgemeinschaft (DFG-Forschergruppe HO 955/2). The calculations were partly done on the IBM SP2 at the LRZ in Munich.

REFERENCES

- [1] F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
- [2] S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. Fujimori, H. Daimon, Y. Ueda, K. Kosuge, and S. Kachi, Phys. Rev. B. **41**, 4993 (1990).
- [3] E. Goering, M. Schramme, O. Müller, R. Barth, H. Paulin, M. Klemm M. L. denBoer and S. Horn, Phys. Rev. B **55**, 4225 (1997).
- [4] V. M. Bermudez, R. T. Williams, J. P. Long, R. K. Reed, and P. H. Klein, Phys. Rev. B **45**, 9266 (1992).
- [5] Takayuki Uozumi, Kozo Okada, and Akio Kotani, J. of Phys. Soc. Jpn. **62**, 2595 (1993).
- [6] J. B. Goodenough, Phys. Rev. **117**, 1442 (1960).
- [7] A. Zylbersztein and N. F. Mott, Phys. Rev. **B 11**, 4383 (1975).
- [8] E. Caruthers, L. Kleinman, and H. I. Zhang, Phys. Rev. B **7**, 3753 (1973).
- [9] C. Sommers, R. de Groot, D. Kaplan, and A. Zylbersztein, J. Phys. Lett. **36**, L157 (1975).
- [10] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, Phys. Rev. Lett. **72**, 3389 (1994).
- [11] V. Eyert, to be published.
- [12] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
- [13] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).
- [14] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW method* (Kluwer Academic Publishers, Boston, 1994).
- [15] S. Y. Savrasov and D. Y. Savrasov, Phys. Rev. B **46**, 12181 (1992).
- [16] C. Sommers and S. Doniach, Solid State Commun. **28**, 133 (1978).

- [17] A. E. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S.R. Barman, K. Maiti, D. D. Sarma, Y. Tokura, and M. Onoda, Phys. Rev B **54**, 5368 (1996).
- [18] D. B. McWhan, M. Marezio, J. P. Remeika, and P. D. Dernier, Phys. Rev. B **10**, 490 (1974).
- [19] J. M. Longo, and P. Kierkegaard, Acta Chim. Scand. **24**, 420 (1970).
- [20] X. Y. Huang (unpublished).
- [21] M. Abbate, F. M. F. de Groot, J. C. Fuggle, Y. J. Ma, C. T. Chen, F. Sette, A. Fujimori, Y. Ueda, and K. Kosuge, Phys. Rev. B **43**, 7263 (1991).
- [22] K. Schwarz, J. Phys. F **16**, L211 (1986).
- [23] I. I. Mazin, D. J. Singh, and C. Ambrosch-Draxl, cond-mat/9806378.

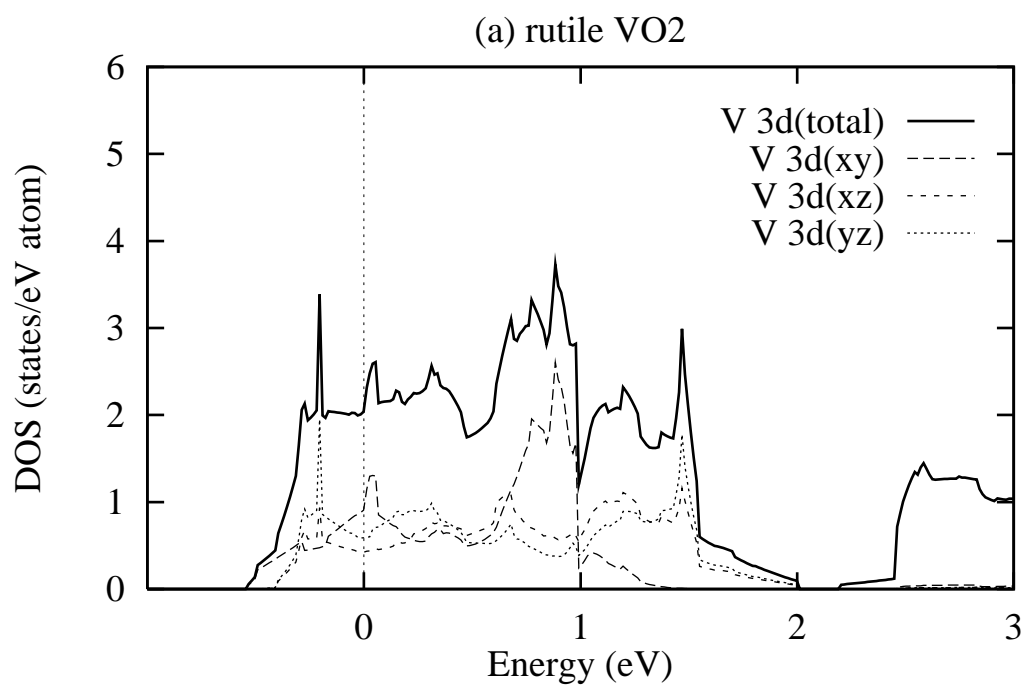
FIGURES

FIG. 1. Partial V $3d$ densities of states (DOS) of VO_2 in (a) the high temperature rutile and (b) the low temperature monoclinic structure, respectively, within the LDA method.

FIG. 2. Band structure of monoclinic VO_2 from (a) LDA and (b) LDA+ U , with $U=4.0$ eV.

FIG. 3. Band gap vs screened (local) Coulomb interaction. A negative "gap" means that an overlap of the $d_{||}$ and the π^* bands.

FIG. 4. Comparison of ultraviolet photoemission data [2] with the calculated DOS of monoclinic (insulating) VO_2 .



(b) monoclinic VO₂

